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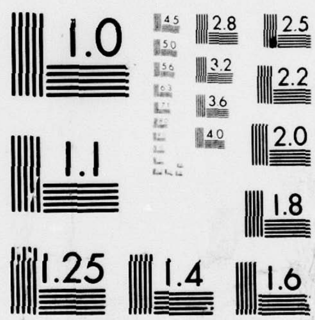

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(6) # The Effect of Halon 1301 Fire Extinguishing Agent on the Response of Combustible Gas Indicators,

(10) W. A. AFFENS

Combustion and Fuels Branch
Chemistry Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A combustible gas indicator (CGI) was tested in combustible vapor-air mixtures with and without the presence of halon 1301 vapors. CGI response to hydrocarbon vapors was reduced on the average of about 30% in the presence of halon 1301 vapors at fire extinguishment concentrations for hydrocarbon type fires (3.7%) and about 45% at inerting concentrations (7.4%). Some filament deterioration was noted in filaments which were exposed to halon vapors. Sensitivity loss for these filaments averaged about 9%.

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CONTENTS

THE EFFECT OF HALON 1301 FIRE EXTINGUISHING

AGENT ON THE RESPONSE OF COMBUSTIBLE GAS INDICATORS

INTRODUCTION

Combustible Gas Indicators (CGI) are widely used to detect flammable atmospheres in coal mines, refineries and other industrial plants, and by the Military (1-11). The common CGI is the "hot wire" type which operates by catalytic oxidation of combustible vapors on a heated metal catalyst filament. Most CGI filaments, including those used by the Navy (6,7), are made of platinum, although other metals are sometimes used for this purpose (1-11).

Questions have been raised by the Navy (12) concerning the possible effects of halon 1301 fire extinguishing agent on CGI instruments which are exposed to these vapors. A CGI might be exposed to Halon 1301 vapors because the Navy uses this agent in some cases to extinguish liquid fuel, oil and hydraulic fluid fires aboard ship (13). After such a fire has been extinguished, it is then necessary to establish whether or not a flammability hazard again exists due to the presence of flammable vapors. A CGI is used for this purpose.

For several reasons, halon 1301 and similar vapors might present problems to CGI operation:

(a) Platinum and other catalysts can be affected adversely or "poisoned" by organic halogen compounds and other contaminants (2-5,9). If this should occur, permanent damage to hot CGI filaments might result and this would impair or destroy their usefulness.

(b) Catalytic oxidation of combustible vapors on the CGI filament might be inhibited by halon vapors; this would result in a reduction of instrument sensitivity and hence low readings.

(c) The higher thermal conductivity of halon vapors might cool the filament relative to that of the air/fuel

Note: Manuscript submitted November 20, 1979.

atmosphere used for calibration of the instrument and this might affect CGI readings.

(d) The CGI is designed and calibrated for operation at ordinary oxygen (air) concentrations. Thus, loss of sensitivity will result if the instrument is used to detect combustible vapors in oxygen-deficient atmospheres (3,4,10). This might be the case if the atmosphere is greatly diluted by inert gases, such as the combustion products resulting from a fire (CO_2 and H_2O vapor) or large concentrations of halon vapors. Although a CGI might give a reasonably accurate indication of the presence of combustible gases when the oxygen concentration has been reduced, it can not be relied upon to detect a flammable ("explosive") mixture in highly oxygen-deficient atmospheres without special adaption (4,10). In the case of atmospheres containing insufficient oxygen for complete oxidation, carbon and other by-products of incomplete oxidation may deposit on the catalyst. The deposit will impede contact of subsequent vapors with the filament surface and thus reduce CGI sensitivity (10).

FLAMMABILITY INDEX

The property of flammable vapor-air mixtures which is measured by the CGI is referred to by various terms: "percent explosiveness" (or "explosiveness"), "explosibility", "percent of lower explosive limit" (or "percent LEL"), "explosivity", and other related terminology (1-11). This property is actually a measure of potential flammability hazard rather than "explosion" hazard which these expressions suggest. For this reason, the expression "Flammability Index" has been suggested as more meaningful for this purpose, and will be used here. Flammability Index (E) is defined (14,15) as the ratio of the fuel vapor concentration in air (C, %v/v) to that at its lower flammability limit (L, %v/v), or E = C/L. Since most CGI instruments read in percent, one may define %E = 100 x E. If the fuel-air mixture is equal to the concentration at the lower flammability limit (C = L), the flammability index is 100%. If %E is equal to or greater than 100%, the mixture is flammable provided the concentration is not so large as to exceed the upper flammability limit. If %E is less than 100%, the mixture is non-flammable.

MEASUREMENT OF FLAMMABILITY INDEX BY THE COMBUSTIBLE GAS INDICATOR

Measurement of flammability index is accomplished by means of a CGI which has been calibrated to read percent flammability index (%E) (or equivalent units, such as "percent of the lower flammability limit" or "percent explosiveness") directly. The CGI operation is based on a platinum detector filament which is heated to a suitable temperature by passing an electric current through it. A typical "hot wire" detector filament operates at about 500°C prior to exposure to combustible vapors (8). Catalytic combustion of the combustible vapors on the filament raises its temperature (and hence its electrical resistance) in proportion to the nature (heat of combustion) and concentration of the combustible vapors. The filament is one arm of a Wheatstone Bridge circuit designed to measure changes in resistance of the filament. The deflection of the meter in the bridge circuit at varying vapor concentrations below the lower flammability limit is substantially linear (2-4), so that it is possible to calibrate the CGI as a function of concentration (C) of a given combustible vapor, or, as is usually the case, the percent flammability index (%E).

CALIBRATION OF THE COMBUSTIBLE GAS INDICATOR

Standard combustible vapors of known concentrations are prepared for the CGI calibration. Ideally, the calibration vapors should be the same or similar to the vapors to be detected later. For example a CGI for detecting methane-air atmospheres should be calibrated against methane-air mixtures.

As a rule, however, CGI instruments are calibrated with air mixtures of n-pentane, or n-hexane, or similar light hydrocarbons, but are then used to detect complex combustible vapor mixtures such as gasoline and the like. If there are large variations in composition and/or molecular weight between the combustibles to be detected and that of the calibration standard (e.g., diesel fuel vapors versus n-pentane), errors may result due to the reduction of CGI response to higher molecular weight vapors (1,8, 16-18).

In order to obtain %E for calibration purposes (%E = 100C/L), it is necessary to know the lower flammability limit (L). Flammability limit data are available in the literature (19-22), or may be determined experimentally if necessary.

HALON 1301

Many halogenated hydrocarbons ("halons") have been investigated over the years, and some of these have been found to be effective for fire extinguishment and/or inerting (23-29). Of the many halons investigated, a few were found to be much more effective than common inert gases such as CO_2 or N_2. The added effectiveness of these halons is attributed to chemical inhibition since it is believed that halon vapors or their decomposition products react with transient combustion products which are necessary for flame propagation (28,30). Of the many halons tested, "halon 1301" (or "1301") has been found to be particularly effective against certain types of fires and has been widely accepted as a fire extinguishing agent (31, 32). It is used by the Navy against Class B (flammable liquids and gases) fires aboard certain ships (13). Several reviews on halon agents can be found in the literature (23,26,27,29).

Chemically, 1301 is liquified monobromotrifluoromethane ($CBrF_3$). Its physical and chemical properties and specification requirements for use as a fire extinguishing agent may be found in the literature (13,30-32). Typical 1301 concentration for fire extinguishment and inerting vary depending on the type of fuel and other conditions (24-30). For liquid hydrocarbon type fires, average minimum concentrations for extinguishment and inerting are about 3.7% and 7.2% respectively (24-30). Present design concentrations for Class B fire extinguishment in the Navy installations is 6%.

EXPERIMENTAL

(a) Combustible Gas Indicator - A "J-W Sniffer" standard portable Model "G" CGI was used, manufactured by Bacharach Instrument Company (7). Two platinum filaments were included in the Wheatstone Bridge circuit, one for "Reference", and the other "Active" for exposure to the

sample. The CGI included variable control knobs for "voltage" and "zero" adjustment. It was powered by eight standard flash light dry cells (Size "D"). Six sets of spare filaments were obtained.

(b) Gas Mixture Preparation System - A manifold system consisting of pressure gauges, vacuum pump, and standard connectors for compressed gas bottles was used. Gas mixtures were prepared manometrically by partial pressure.

(c) Compressed Gas Supply - Cylinders of compressed air and halon 1301 were attached to the manifold system.

(d) Hydrocarbon Fuel - Phillips 99 mole percent was used for both calibration and the halon experiments.

(e) Preparation of Vapor Mixtures - Mixtures were prepared in standard 100 cu. in. (1.64 liters) steel sample cylinders ("bottles") fitted with standard connector fittings and valves. The cylinders were first evacuated by means of the vacuum pump in the manifold system. The valve was then closed and the bottle was disconnected from the system. A rubber septum was connected to the connector fitting, and measured quantities of liquid pentane were added to the bottle by means of a hypodermic syringe and a fine needle through the septum. The desired quantities of halon 1301 (if required) and air were then admitted using the manifold system to give a total pressure of 215 psia (14.63 atm.). Three sets of three bottles each (total of nine) were used. Each set of three contained 0.50-, 0.75-, and 1.00-ml liquid n-pentane respectively. The first set contained no halon 1301, the second and third sets contained 3.7% and 7.4%, respectively. These halon concentrations were intended to approximate the levels necessary for fire extinguishment and inerting, respectively. The pentane vapor concentrations (C) were calculated to be 0.44%, 0.65% and 0.87% respectively by means of the ideal gas law. Since the lower flammability limit of (L) of n-pentane at 25°C is 1.4% (19-22), the corresponding flammability indices (%E) were estimated to be 31%, 47%, and 62% respectively. Compositions of the n-pentane-halon 1301-air mixtures are shown in Table I. Mixtures 1, 2, and 3 were used for calibration.

(f) Combustible Gas Indicator Response - The nine bottles were used in sequence to measure CGI readings (R). The instrument was purged with air after each bottle. The calibration mixtures were run before and after each series of runs in order to monitor effects on sensitivity. After

each series of tests, a fresh new filament was inserted into the CGI, and the entire series of runs repeated for three different filaments.

The first series was also run with a fresh filament, since the initial filament which came with the CGI, burned out in use shortly after the initial exposure to the halon vapors. This filament failure, however, may be a coincidence and not due to halon exposure since filaments often fail in normal use. An additional filament was tested after the halon experiments were completed to determine the effects of normal use on filament sensitivity. The last filament was left "on" for over a half hour in the presence of n-pentane-air vapors (no halon) and again checked for sensitivity. The half-hour time was judged to be in excess of the hydrocarbon vapor exposure time during the halon experiment. No change in sensitivity was observed as a result of this exposure.

(g) CGI Sensitivity - The sensitivity (S) of a CGI is defined as the ratio of the instrument reading (R) to that of the flammability index (E) of the gas mixture being tested:

$$S = R/E$$

If the instrument reading (percent of the lower flammability limit) actually corresponds to the flammability index (%E) of the mixture, $S = 1$. If a CGI has linear response to varying vapor concentration (or varying %E) of similar hydrocarbon/air mixtures, S will be constant for that system. It is possible to determine an average S by plotting R versus E for several hydrocarbon concentrations and determining the slope of the best straight line through the data. S is useful as a means of monitoring the effect of halon 1301 (or other vapors) on CGI response.

RESULTS

Results are given in Table II - IV and in Figures 1 and 2. Direct CGI readings (R) are shown in Table II and sensitivities (S) in Table III. The data in Table III are averaged for both individual filaments and also for the filaments as a group. Average sensitivity losses are given in Table IV. A plot of average CGI readings versus flammability index is shown in Figure 1, and a plot of average loss of sensitivity versus halon 1301 concentration is shown in Figure 2.

The curves in Figure 1 are all linear as had been expected, but reductions in response can be seen in the halon atmospheres (curves "C" and "D") relative to that of the halon-free results (curve "A"). The average sensitivities obtained from the slopes of these curves agree with the calculated values shown in Table III. The curve in Figure 2 shows increased loss of sensitivity with increasing halon concentrations.

The readings and sensitivity values of the halon-free mixtures show loss of sensitivity before and after exposure to halon atmospheres. This is also shown in Figure 1 (curves "A" and "B").

CONCLUSIONS

The results indicate that halon 1301 at typical concentrations used for fire extinguishment of hydrocarbon fires has two types of effects on CGI response: filament deterioration and loss of CGI sensitivity in the presence of halon vapors.

(a) <u>Filament Deterioration</u> - On the average, there was about a 9% loss of sensitivity in CGI filaments as a result of previous exposure to halon 1301 vapors, as is shown in Table IV. One filament (data not included here) burned out after halon exposure. However, since filaments fail in normal use from time to time, this may not be significant. However, extended exposure to halon vapors may shorten filament life in addition to reducing sensitivity.

(b) <u>CGI Sensitivity in Halon 1301 Atmospheres</u> - The data in the tables and figures show significant reduction of CGI response and sensitivity in the presence of halon 1301 vapors. This suggests that the halon 1301 interferes with the catalytic oxidation of hydrocarbon vapors. Since the reduction in sensitivity is over 30% at 3.7% halon 1301 (Table IV), and since the sensitivity continues to fall with increasing halon concentration (Figure 2), CGI reliability in halon 1301 atmospheres is open to serious question.

RECOMMENDATIONS

(1) Combustible gas indicators should only be used in halon 1301-free atmospheres.

(2) If halon 1301 has been used to extinguish a Class "B" fire in a given compartment, the compartment should be purged of halon before the CGI is used. A halon detector, such as is used in the refrigeration industry, might be useful for this purpose (perhaps with modification).

(3) A CGI should be recalibrated frequently against standard calibration mixtures, particularly after use in contaminated atmospheres.

(4) Spare filaments should be available for filament replacement when necessary.

(5) CGI should not be used in very oxygen-deficient atmospheres, since CGI sensitivity will be reduced. Also, catalytic oxidation in very oxygen deficient atmospheres may be incomplete so that carbon and/or products of incomplete oxidation may deposit on the filament catalyst and cause permanent loss of sensitivity.

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Table I - Composition of n-Pentane-Halon 1301-Air Mixtures

Mixture	Concentration (%v/v) n-Pentane* (C)	Concentration (%v/v) Halon 1301	Flammability Index %E = 100C/L
1	0.44	0	31
2	0.65	0	47
3	0.87	0	62
4	0.44	3.7	31
5	0.65	3.7	47
6	0.87	3.7	62
7	0.44	7.4	31
8	0.65	7.4	47
9	0.87	7.4	62

* - Lower Flammability Limit (L, %v/v) = 1.4%

Table II - Effect of Halon 1301 on CGI Readings

Mixture	Halon 1301(%v/v)	Flammability Index %E	CGI Reading (R, %) Filament Number 1	2	3	Average
1	0	31	43	48	50	47 ± 3
2	0	47	70	77	75	74 ± 3
3	0	62	88	94	98	93 ± 4
4	3.7	31	28	33	40	34 ± 5
5	3.7	47	45	55	50	50 ± 4
6	3.7	62	55	63	72	63 ± 7
7	7.4	31	25	22	25	24 ± 1
8	7.4	47	42	42	48	44 ± 3
9	7.4	62	50	53	60	54 ± 4
1*	0	31	41	42	45	43 ± 2
2*	0	47	68	63	70	67 ± 3
3*	0	62	85	82	87	85 ± 2

* - After exposure to halon vapors

Table III - Effect of Halon 1301 on CGI Sensitivity

Mixture	Halon 1301(%v/v)	Flammability Index (%E)		Sensitivity (S = R/E) Filament Number 1	2	3	Average
1	0	31		1.39	1.55	1.61	1.52 ± 0.09
2	0	47		1.49	1.64	1.60	1.58 ± 0.06
3	0	62		1.42	1.52	1.58	1.51 ± 0.07
			Average	1.43	1.57	1.60	1.53 ± 0.07
4	3.7	31		0.90	1.06	1.29	1.08 ± 0.10
5	3.7	47		0.96	1.17	1.06	1.06 ± 0.09
6	3.7	62		0.89	1.02	1.16	1.02 ± 0.11
			Average	0.92	1.08	1.17	1.06 ± 0.10
7	7.4	31		0.81	0.71	0.81	0.78 ± 0.05
8	7.4	47		0.89	0.89	1.02	0.93 ± 0.06
9	7.4	62		0.81	0.85	0.97	0.88 ± 0.07
			Average	0.84	0.82	0.93	0.86 ± 0.06
1*	0	31		1.32	1.35	1.45	1.38 ± 0.06
2*	0	47		1.45	1.34	1.49	1.43 ± 0.06
3*	0	62		1.37	1.32	1.40	1.37 ± 0.03
			Average	1.38	1.39	1.45	1.40 ± 0.05

* - After exposure to halon vapors

Table IV - Average CGI Sensitivity Losses in Halon 1301 Atmospheres

Mixtures	Halon 1301(%v/v)	Sensitivity (S)	Loss (ΔS)	Relative Loss (%ΔS)
1,2,3	0	1.53	-	-
4,5,6	3.7	1.06	0.47	31%
7,8,9	7.4	0.86	0.67	44%
1,2,3*	0	1.40	0.13	9%

* - After exposure to halon vapors

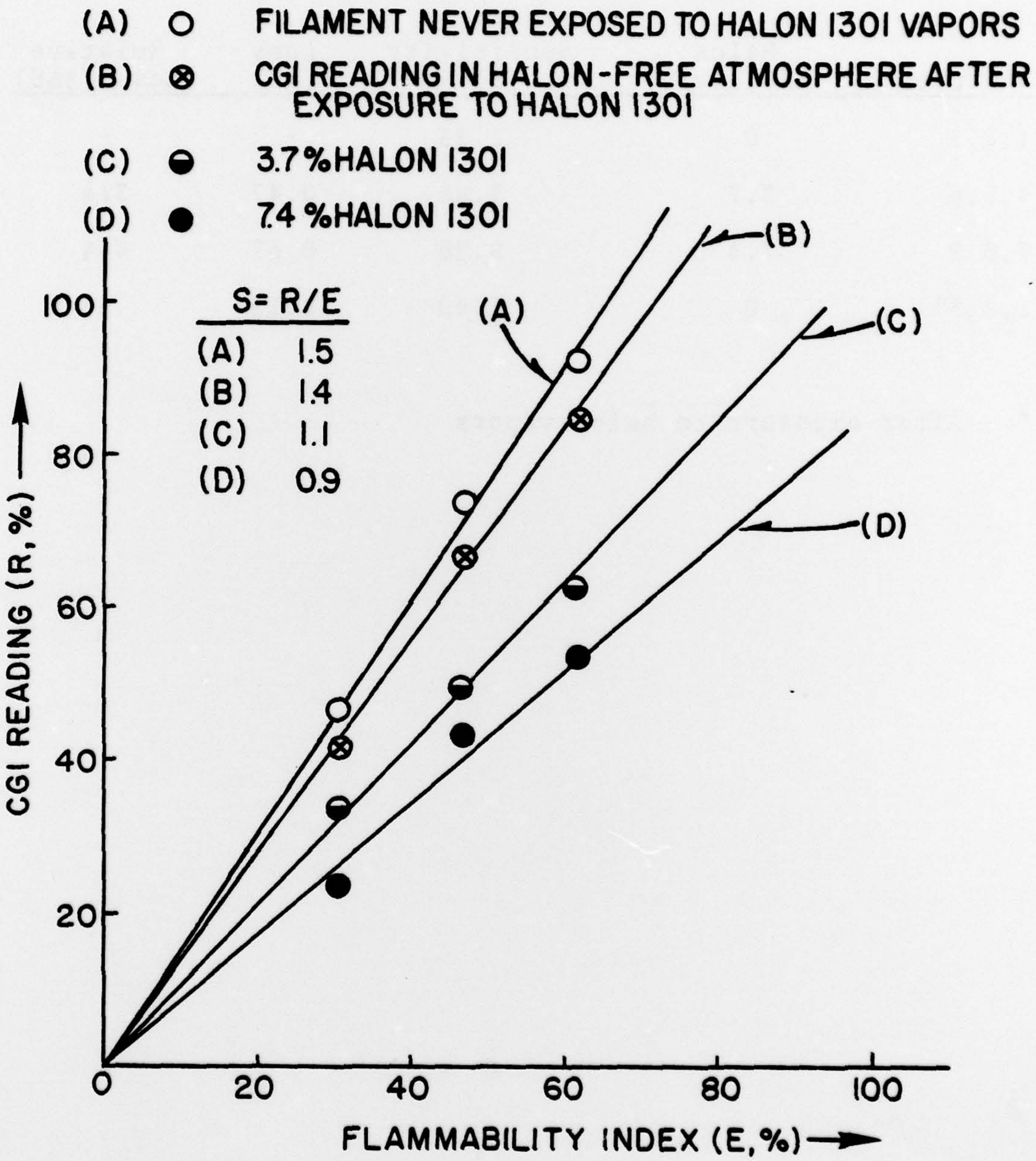

Fig. 1 — Effect of halon 1301 on CGI response

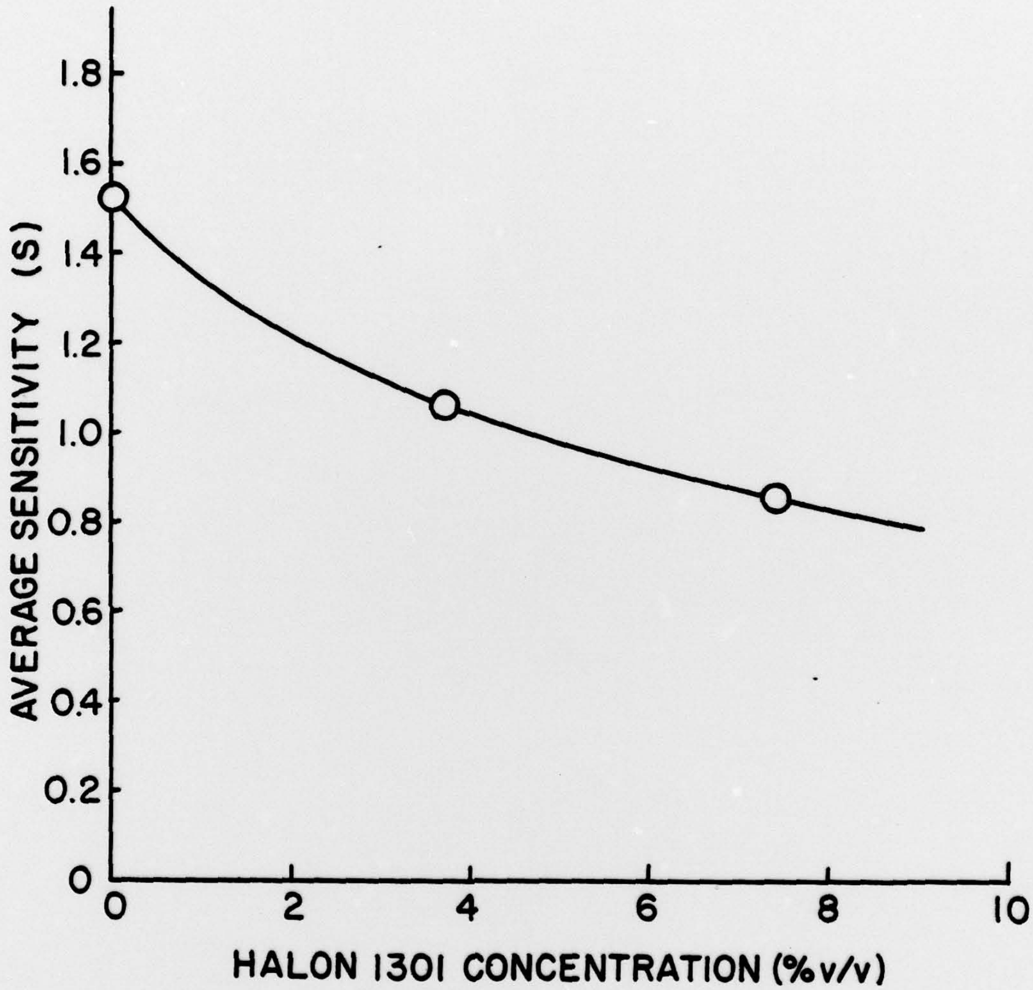

Fig. 2 — Effect of halon 1301 concentration on CGI sensitivity